



April 27, 2019

TO: Elizabeth D. Lamerson and citizens of Pike County, Ohio

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IN COLLABORATION WITH: Scott C. Szechenyi, M.S., Independent Consultant^b, BS '97, MS '01, Northern Arizona University

SUBJECT: Investigation of anthropogenic uranium, neptunium, and plutonium in environmental samples near Piketon, Ohio

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SUBMITTED BY:

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Summary. A *pro bono*, public interest study has been completed to investigate potential sources of uranium (U), neptunium (Np) and plutonium (Pu) in environmental samples from the vicinity of Piketon, OH. The authors collaborated with a local community member, and analyzed the samples at Northern Arizona University, using modern nuclear forensics approaches.

The principal questions to be addressed were: a) can non-natural uranium be found in the local environment, and b) can non-weapons-testing fallout neptunium and plutonium be similarly found? We assumed the null hypotheses that all environmental U is naturally occurring, and that all Np-Pu stems from Cold War-era nuclear weapons testing fallout.

The data showed that non-natural U, and non-fallout Np and Pu are systematically present in many locations; accordingly, we tested the alternative hypotheses that, the Portsmouth Gaseous Diffusion Facility (PORTS) are the explanatory sources therein. We observed, using isotope mixing plots, that the U, Np, and Pu are reasonably explained using fallout and PORTS/Paducah end-members described in two DOE-funded studies (Moody, 1995; Kelley *et al.*, 1999).

Several specific findings are as follows:

- 1) Enriched U is found in surface waters, sediments, and interior dusts. This enriched U also contains ^{236}U , a known component of “recycled U” that was processed at PORTS. The environmental samples exhibiting enriched U have compositions consistent with mixing between natural U and PORTS U (Moody, 1995).
- 2) Non-fallout ^{237}Np and Pu isotopes are also found in bed sediments, suspended sediments, and interior dusts. These transuranic elements are known contaminants in feed material used at PORTS and the Paducah facilities. The environmental samples exhibiting non-fallout Np and Pu are consistent with mixing between global “stratospheric fallout” Np-Pu (Kelley *et al.*, 1999), and material sampled from the Paducah and Portsmouth Gaseous Diffusion Plants (Moody, 1995).
- 3) The study consistently found non-fallout ^{237}Np in suspended sediments of an unnamed creek that is draining a landfill construction area that is currently being worked. These results indicate a probable source of ^{237}Np in surface materials within the creek’s drainage basin.
- 4) We have also encountered enriched uranium in interior spaces at a local school, and in the attic dust sampled from various residents, including a residence that was constructed in 2007. These findings point to recent/ongoing airborne releases, as opposed to legacy contamination dating to the 20th century.
- 5) The assembled evidence indicates, with a reasonable degree of scientific certainty, that emissions from the PORTS facility account for the anthropogenic contents of U, Np, and Pu encountered in environmental samples from the Piketon vicinity.

Introduction. The purpose of this project was to investigate environmental samples supplied to the authors by Elizabeth D. Lamerson, as part of a study of the possible presence of anthropogenic U (uranium), neptunium (Np) and plutonium (Pu) in the environment. The study focused on environmental samples Ms. Lamerson gathered from the proximity of Piketon, Ohio. The principal questions addressed were: A) *can non-naturally occurring U be identified in the local environment?* and B) *can Np and Pu be identified in the local environment that originate from source(s) other than nuclear weapons testing fallout?* Our study used scientifically sound, legally defensible methods that are well known and accepted in the field of nuclear forensics, which mirror the approaches used by qualified laboratories/scientists throughout the world.

Methods. Media sampled/analyzed include: i) surface soils; ii) aquatic sediments and surface water samples from local creeks and the Scioto River; iii) “swipe” samples collected from un-inhabited interior spaces; and iv) bulk dust samples vacuumed or hand-gathered from un-inhabited interior spaces. Ms. Lamerson and other community members collected samples from public areas; additional samples were collected with appropriate access and permissions from private property. ***No samples were acquired from US Government property.*** All samples from private/residential property are de-identified as to ownership and geography, to respect the absolute confidentiality and privacy of the cooperating citizens. The authors will not reveal this location/identity information.

No attempt has been made to measure U concentrations, and accordingly, no inferences are made nor implied regarding this element’s concentrations in comparison to established maximum contaminant levels (MCL’s). While this has not been pursued herein, the authors acknowledge the importance of this undertaking in future studies.

The present focus on isotope (atom) ratios enables a sensitive and robust comparison between natural vs. anthropogenic (e.g., isotopically enriched or depleted) sources of uranium in many types of environmental or biological samples. All results were measured by quadrupole inductively coupled plasma mass spectrometry (Q-ICPMS), following established, well-known chemical preparation and instrumental measurement strategies (e.g., Ketterer *et al.*, 2000a, 2000b, 2003). For the element uranium, the ratios measured include: $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$. These dimensionless values represent the actual ratios of the number of atoms of the specified masses, present in the sample under investigation. The measurement of these three U isotope ratios permits the detection of relatively small deviations from natural U found in the Earth’s crust (*via* deviations in $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$), as well as the detection of small inputs of “recycled uranium”.

Using $^{236}\text{U}/^{238}\text{U}$ ratios, one can detect the presence of small additions of U recovered from Pu production reactors, as ^{236}U is synthesized by neutron capture processes therein. In situations where enriched or depleted U contains a “recycled uranium” component, the detection of ^{236}U is itself a potentially sensitive measure of such anthropogenic inputs, as ^{236}U is virtually absent in Nature, and only small amounts can be accounted for by nuclear weapons testing fallout (Ketterer *et al.*, 2013). Depleted uranium used in military applications commonly contains ^{236}U (Lloyd *et al.*, 2009; Bu *et al.*, 2017) and it follows that the associated enriched U produced in the same isotope separation processes, will also contain significant levels of ^{236}U .

For Np and Pu, the actual atom concentrations of ^{237}Np , and the activities of $^{239+240}\text{Pu}$ were measured, along with the atom ratios $^{237}\text{Np}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$. As is the case with the U results, the Np-Pu isotope ratios permit analogous, robust comparisons between baseline “stratospheric fallout” vs. non-fallout sources (e.g., the contaminants present in recycled U). The basis for our data interpretations of the Np-Pu results is as described by Kelley *et al.* (1999), a DOE-funded study that was conducted at Pacific Northwest National Laboratory. Our laboratory methodologies for Np and Pu measurements followed sample preparation and Q-ICPMS-based procedures discussed elsewhere (Ketterer *et al.*, 2004, Ketterer and Szechenyi, 2008). The Np-Pu results for selected samples were confirmed by Q-ICPMS at an external laboratory (Prof. José Luis Más, CITIUS, Universidad de Sevilla), in order to affirm the major inferences from our own lab work.

Results. The analytical results obtained in this study are presented in Table 1 (U) and Table 2 (Np-Pu). These tables display the above-mentioned ratios for the elements U, Np, and Pu.

For purposes of inferring the presence of anthropogenic U and/or non-weapons test fallout Np-Pu, the measured ratios should be compared to the following benchmarks:

Ratio	Expected in Nature and/or contemporary baseline
$^{234}\text{U}/^{238}\text{U}$	0.000055 (affected by ^{234}U - ^{238}U disequilibria)
$^{235}\text{U}/^{238}\text{U}$	0.0072527 (varies within a $\sim 0.2\%$ relative range <i>via</i> natural fractionation processes)
$^{236}\text{U}/^{238}\text{U}$	$\sim 10^{-10}$ in Nature; influenced by fallout (Ketterer <i>et al.</i> , 2013)
$^{237}\text{Np}/^{239}\text{Pu}$	0.48 ± 0.07 (Kelley <i>et al.</i> , 1999)
$^{240}\text{Pu}/^{239}\text{Pu}$	0.180 ± 0.014 (Kelley <i>et al.</i> , 1999)

It is obvious, from a cursory examination of Tables 1 and 2, that “anthropogenic U” and “non-fallout Np-Pu” are pervasive in the environment surrounding Piketon. This generates the obvious hypothesis, namely, that the local Portsmouth Gaseous Diffusion Facility (PORTS) facility is the explanatory source of the U-Np-Pu contamination. In order to test this hypothesis, the interpretations of these results, and inferences provided, will follow in the next sections of the report.

End Members. A previous study of PORTS samples was conducted as part of a larger counter-forensics program (PUBLIC); an unlimited distribution report was published by Lawrence Livermore National Laboratory (Moody, 1995). The major findings of the Moody report are discussed herein to add context and to aid interpretation of the present Piketon datasets. The Moody (1995) study conducted an interrogation of the U-Np-Pu signatures present during the ~ 1994 sampling from within process areas at the PORTS site. The Moody (1995) U-Np-Pu signatures can serve as a reasonable “end-member”, representing a snapshot of the potential PORTS releases in the environment; the other end members would consist of natural U, and the weapons-testing fallout Np-Pu signature. One must

bear in mind that the Moody samples are only a single sampling event, at one point in time and limited in scope/space, over a decades-long history of a large-scale facility.

It is common practice in the isotope geosciences to interpret mixing processes using “mixing plots”, typically consisting of two ratios bearing a common denominator. Herein, we make use of mixing plots of $^{234}\text{U}/^{238}\text{U}$ vs. $^{235}\text{U}/^{238}\text{U}$, and $^{237}\text{Np}/^{239}\text{Pu}$ vs. $^{240}\text{Pu}/^{239}\text{Pu}$.

The null hypothesis (H_0) for uranium in an unknown environmental sample is that the $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ are congruent with naturally occurring uranium; in other words, no other end member need be invoked to explain the observed isotope composition. On a mixing line, samples that support H_0 will cluster, within measurement uncertainty, of naturally occurring U ratios; samples that are statistically distinguishable on the plot from the H_0 cluster will be immediately apparent, and thus, one rejects H_0 . The alternate hypothesis, H_1 , is that the sample contains an anthropogenic component of enriched or depleted U, from an external source that requires a plausible explanation.

In a similar manner, H_0 for Np-Pu is that the source of these elements, if even detectable, is from nuclear weapons testing fallout, deposited globally, mainly during the 1950's and 1960's. The Kelley *et al.* (1999) study is the authoritative paper on the Np-Pu characteristics of global fallout. The Kelley study also discusses the uses of ^{237}Np - ^{239}Pu - ^{240}Pu mixing diagrams in the detection of other Np-Pu sources. The H_1 herein is that a non-fallout Np-Pu source is present, analogous to above discussion regarding the U hypotheses.

In any two-ratio, common-denominator mixing diagram, simple binary mixtures of two components plot along a straight line segment, spanning the end members, as was observed for global fallout mixed with Chernobyl debris (e.g., as discussed in Ketterer and Szechenyi, 2008). Additional components may, coincidentally, fall along the mixing line, although more commonly, fall well away from the line. Lastly, it is important to keep in mind that correlation does not prove causation when interpreting mixing plots, although often, there is only one realistic explanation for two-component mixing behavior.

The 1995 Moody study is important, because it defines the composition of PORTS, an important local source of environmental actinides acknowledged by the US Government (e.g., DOE, 2019). Legacy and/or contemporary/ongoing emissions from PORTS would alter the H_0 U-Np-Pu environment signatures, leading to rejection of either/both the U or Np-Pu null hypotheses for individual offsite samples. If H_1 is accepted, the Moody signatures allow one to ascertain whether PORTS is the explanatory source.

Moody's Project PUBLIC (Portsmouth/Paducah Uranium Barrier: Livermore Investigative Campaign) analyzed three samples obtained from inside the PORTS facility; the U-Np-Pu compositions of these were determined through rigorous analytical work at a DOE-funded lab (Lawrence Livermore National Laboratory), and therefore, there is no ambiguity regarding the PORTS samples' authenticity. Moody (1995) also characterized two samples from the Paducah Gaseous Diffusion Facility, a site which delivered pre-enriched feed material for further enrichment at PORTS. The Moody samples also varied in U isotope composition, and generate a mixing plot, shown in Figure 1.

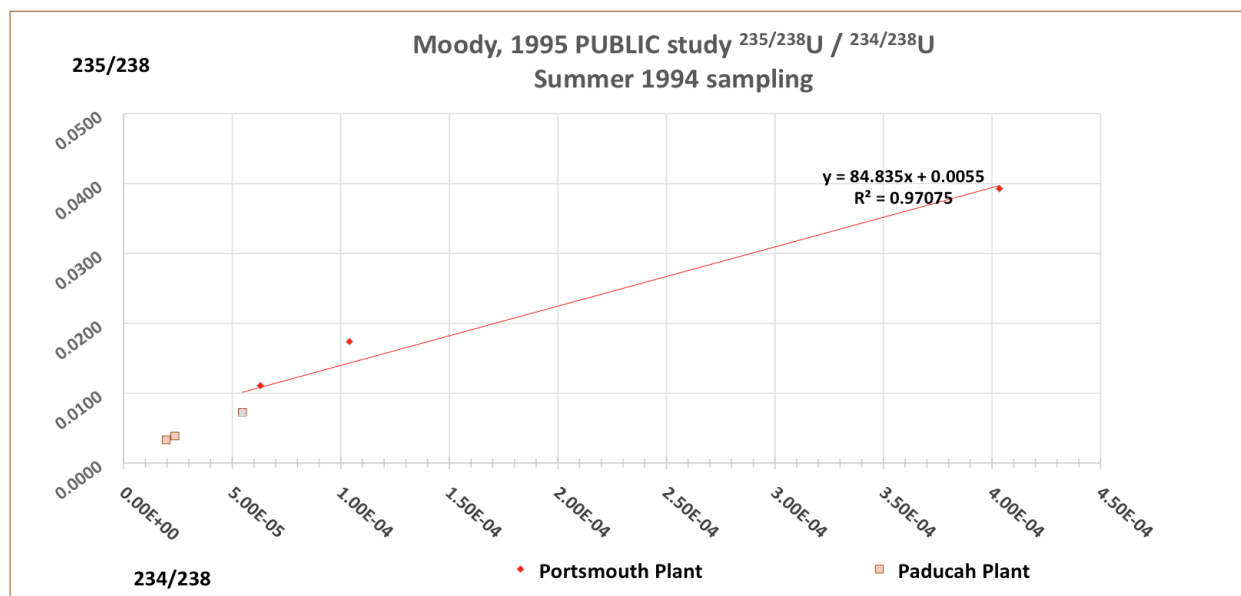


Figure 1. ^{234}U - ^{235}U - ^{238}U mixing diagram of PORTS samples mixed with natural composition uranium, from data reported by Moody, 1995, UCRL-ID-119658. The trendline has been defined for natural and PORTS samples. Paducah plant samples are plotted (but not included in trendline regression), as the Paducah cascade is considered to be one of the PORTS feedstock sources. An interesting observation by Moody indicates a slightly depleted uranium signature in samples analyzed from the Paducah plant. Natural uranium is used as the left-hand end member.

Uranium sources. Using naturally occurring U, global fallout Np-Pu, and the Moody U-Np-Pu signatures as potential end-members, we turn to examining whether the Piketon-vicinity environmental samples exhibit: A) rejection of either H_0 ; and B) mixing patterns that point to the Moody PORTS U-Np-Pu signatures as an explanatory source. A series of Figures (2 through 5) compare the observed isotope compositions vs. U end-members and the Moody mixing line.

Figure 2 illustrates the U isotope compositions of dust samples collected from the interior of a local Piketon-vicinity school. The dust samples, collected as “swipes”, using absorbent cloths resembling “baby wipes” exhibit the following: A) the H_0 is rejected for at least four of the samples (red triangles) and therefore, ***these dust samples from the school must contain at least some added enriched U component***; and B) there exists a fairly consistent two-component mixing relationship. The Moody 1995 trendline is overlain for comparison.

Analogous comparisons for uranium isotope compositions are provided, using the data of Table 1, for samples from the Scioto River (Figure 3), Piketon-vicinity creeks and drainages (Figure 4), and for dusts and soils collected from Piketon-vicinity residences (Figure 5). In all cases, similar findings are evident: H_0 is repeatedly rejected, for many data points, and the observed patterns closely follow two-component mixing lines. Each comparison leads to the immediate conclusion, that ***many of the environmental samples contain at least some added enriched U component***.

In reference to uranium isotope compositions, some important findings can be garnered from the U isotope compositions of specific samples reported in Table 1. Samples 55 and 77 represent attic dust “swipes” collected in two independent sampling events from one local residence; according to the owners, the residence was constructed in 2007. Samples 55 and 77 exhibit $^{235}\text{U}/^{238}\text{U}$ of 0.00799 and 0.00896, respectively. **These results point to the existence of recent, or contemporary/ongoing transport processes that have resulted in deposition of enriched U at this residence.** Accordingly, the contamination cannot be accounted for by legacy emissions that occurred prior to 2001, when routine enrichment operations terminated at PORTS.

Selected samples demonstrate that the enriched U also contains ^{236}U . The long-lived ^{236}U isotope is found at extremely low abundances in Nature; background, pre-nuclear era $^{236}\text{U}/^{238}\text{U}$ are $\sim 10^{-10}$ or lower. Small amounts of ^{236}U are also associated with nuclear weapons testing fallout, and stratospheric fallout is characterized by a $^{236}\text{U}/^{239}\text{Pu}$ atom ratio of ~ 0.2 (Ketterer *et al.*, 2013). Fallout-derived $^{236}\text{U}/^{238}\text{U}$ are commonly $\sim 10^{-7}$ or less, and are controlled by i) fallout inventory and ii) crustal ^{238}U concentrations. In contrast, the overarching pattern of the Piketon-vicinity environmental samples is that they exhibit detectable ^{236}U , wherever sufficiently elevated $^{235}\text{U}/^{238}\text{U}$ ratios are present, provided that U signal levels in the mass spectrometer allow reliable measurement of $^{236}\text{U}/^{238}\text{U}$.

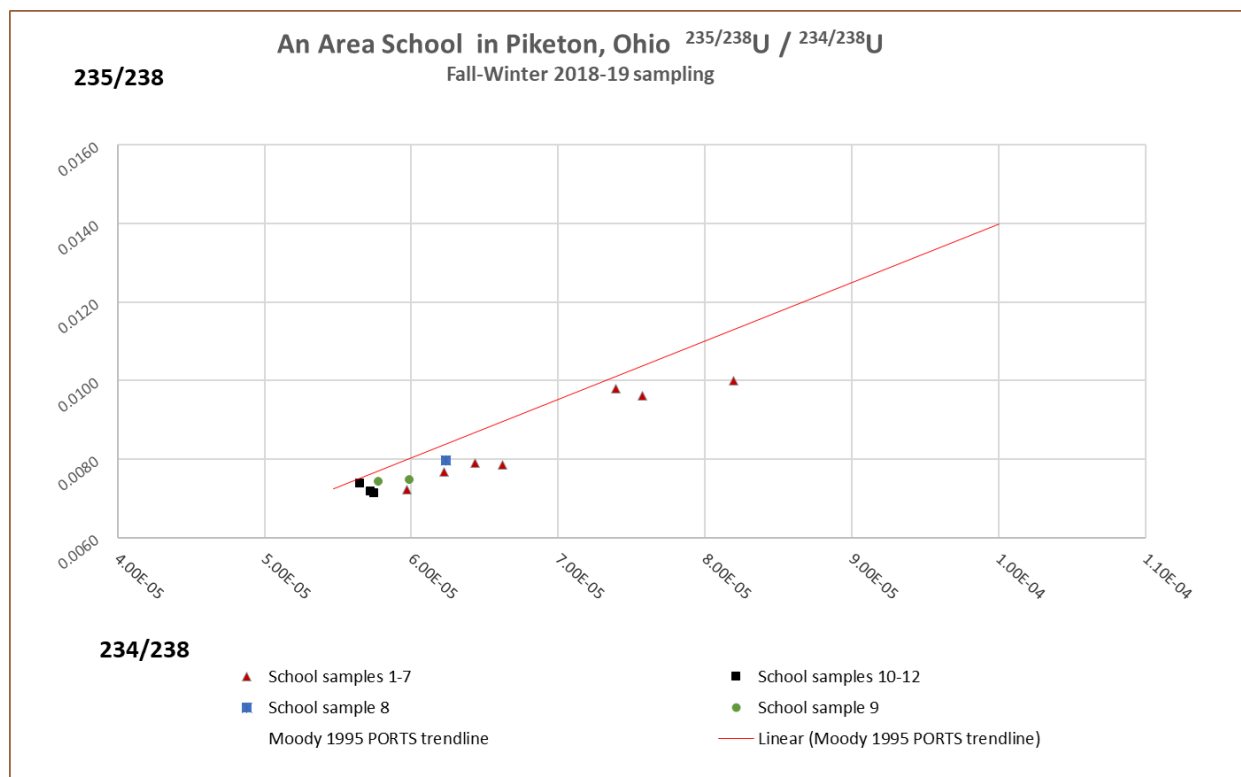


Figure 2. ^{234}U - ^{235}U - ^{238}U mixing diagram of samples collected at a Piketon-vicinity school in Fall/Winter 2018-2019. The mixing line of PORTS sample data from Moody (1995) is included for comparison.

The presence of ^{236}U can be most reliably detected when $^{235}\text{U}/^{238}\text{U}$ is grossly elevated; a case in point can be seen in dissolved U in Little Beaver Creek, Big Beaver Creek, and in the

Scioto River. Referring to Table 1, Sample 45 (Little Beaver Creek, downstream) exhibited $^{235}\text{U}/^{238}\text{U} = 0.0224$ and $^{236}\text{U}/^{238}\text{U} = 0.000075$; Sample 47 (Big Beaver Creek, downstream) had $^{235}\text{U}/^{238}\text{U} = 0.0218$ and $^{236}\text{U}/^{238}\text{U} = 0.000065$. The ^{236}U -bearing enriched U is also found downstream in the Scioto River ($^{235}\text{U}/^{238}\text{U} = 0.0199$ and $^{236}\text{U}/^{238}\text{U} = 0.000065$). We note that these specific samples plot close to the Moody mixing lines (Figures 3 and 4). **The implied source of this ^{236}U and elevated $^{235}\text{U}/^{238}\text{U}$ in surface waters is the permitted outfalls and/or non-point discharges from the PORTS facility.** Our findings confirm the US DOE's previous findings of dissolved enriched uranium in these same locations (DOE, 2014). The latter study estimated the total 2014 outfall discharges from PORTS to be ~ 14 kilograms, which further supports our findings in these surface waterways.

Other mass spectrometric techniques, such as triple quadrupole ICPMS, or accelerator mass spectrometry (AMS) are better suited than Q-ICPMS for measuring low-abundance ^{236}U (e.g., Bu *et al.*, 2017). It is, therefore, technically feasible to trace the transport of this PORTS-derived dissolved U contamination, even after large dilution, downstream into the Ohio River watershed.

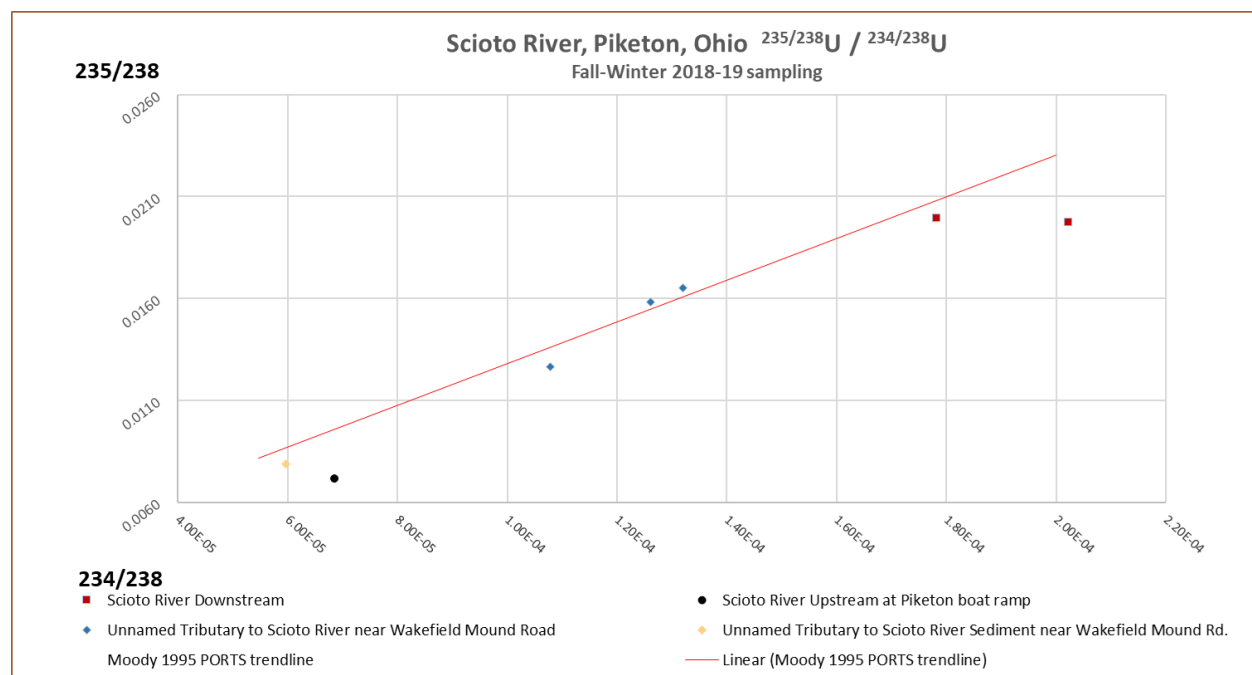


Figure 3. ^{234}U - ^{235}U - ^{238}U mixing diagram mixing diagram of water and sediment samples collected from the Scioto River in Fall/Winter 2018-2019. The mixing line of PORTS sample data from Moody (1995) is included for comparison.

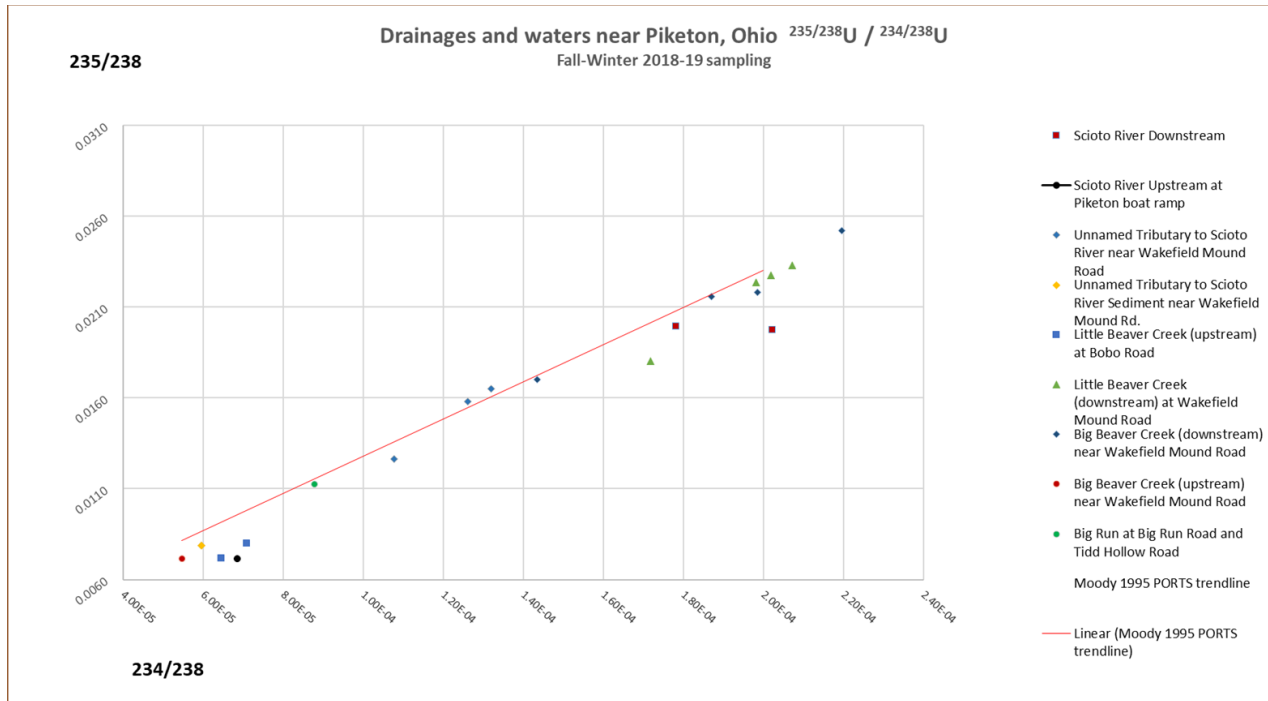


Figure 4. ^{234}U - ^{235}U - ^{238}U mixing diagram of water and samples collected from Piketon-vicinity drainages in Fall/Winter 2018-2019. The mixing line of PORTS sample data from Moody (1995) is included for comparison.

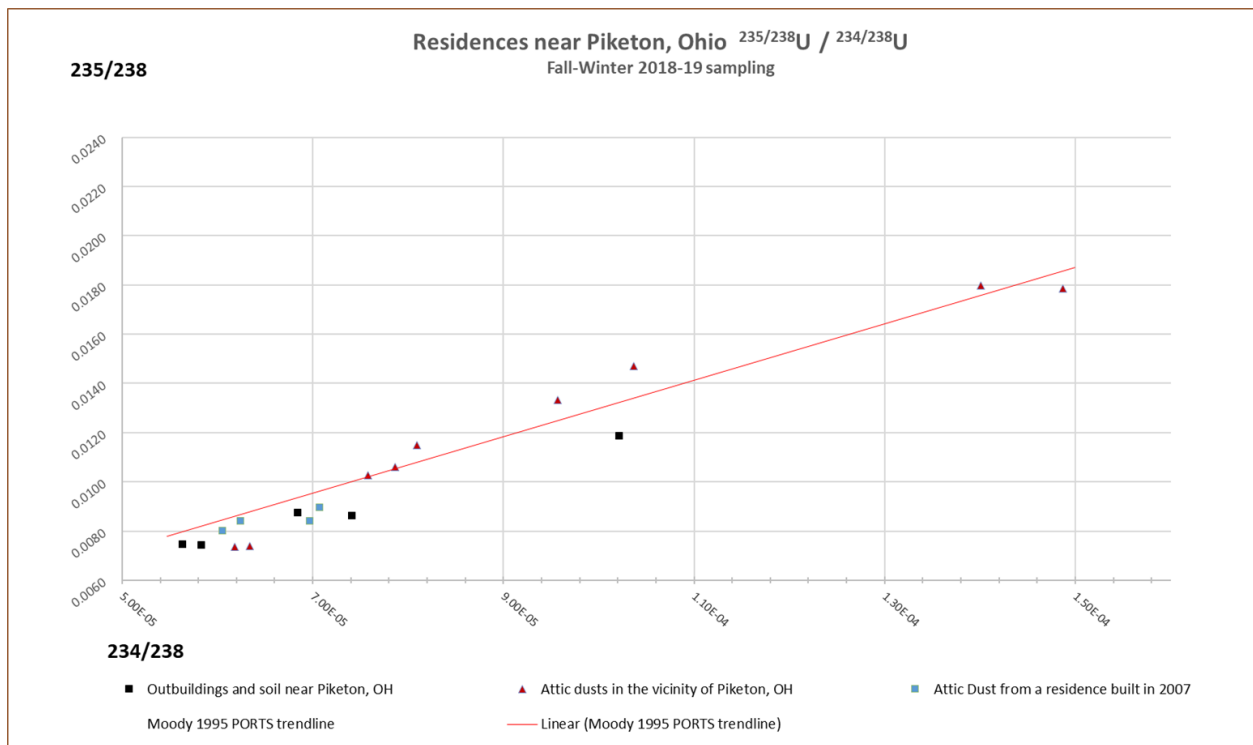


Figure 5. ^{234}U - ^{235}U - ^{238}U mixing diagram of soil and dust samples collected from residences near Piketon-vicinity in Fall/Winter 2018-2019. The mixing line of PORTS sample data from Moody (1995) is included for comparison.

Though not presented in this report, our examination of the U isotope results shows that $^{236}\text{U}/^{238}\text{U}$ vs. $^{235}\text{U}/^{238}\text{U}$ two-component mixing behavior is present. This implicit $^{236}\text{U}/^{238}\text{U}$ - $^{235}\text{U}/^{238}\text{U}$ mixing pattern cannot be explained by mixing between crustal (natural) U and weapons-test fallout; instead, the source of the ^{236}U is “recycled U”.

During the Cold War era, the US Government was concerned with an impending shortage of U metal, and “recycled” U was recovered from Pu production reactors, and the recovered U was blended with primary ore-extracted U feed. Accordingly, most feed to the US’s gaseous diffusion plants contained ^{236}U , a practice that commenced in the 1950’s. The “recycled U” also brings along other concomitants (^{99}Tc , ^{237}Np , and Pu isotopes) that entered the gaseous diffusion process plants. The ^{99}Tc and “transuranics” represent unintended contaminants in the gaseous diffusion process, and their chemical behaviours are significantly different from U in the gaseous diffusion separation chemistry of UF_6 (g). The Moody (1995) study revealed the presence of ^{236}U (as well as ^{237}Np and Pu isotopes) in DOE-authenticated PORTS samples; therefore, ***it is beyond question that ^{236}U , ^{237}Np , ^{239}Pu , and ^{240}Pu are specifically associated with PORTS facility processes.***

Neptunium and plutonium sources. As previously stated, the Kelley *et al.* (1999) DOE study is the authoritative source describing the expected Np-Pu isotope compositions of weapons-testing “stratospheric” fallout found globally. Kelley *et al.* (1999) used plots of $^{237}\text{Np}/^{239}\text{Pu}$ vs. $^{240}\text{Pu}/^{239}\text{Pu}$ to examine mixing of the two dominant North American sources of fallout, namely, “stratospheric” and Nevada Test Site fallout. The Kelley paper also states that non-fallout sources are immediately apparent on these three-isotope mixing diagrams.

The results for the determination of ^{237}Np mass concentrations, $^{239+240}\text{Pu}$ activities, and the atom ratios $^{237}\text{Np}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ are presented in Table 2. What is immediately apparent is that ***many of the $^{237}\text{Np}/^{239}\text{Pu}$ ratios grossly exceed the expectations for global (stratospheric) fallout*** as reported by Kelley *et al.* (1999). It is also quite evident that sediments obtained from Little Beaver Creek, Big Beaver Creek, and the Scioto River, all exhibit ***elevated ^{237}Np mass concentrations, that are unrealistic for stratospheric fallout*** (e.g., refer to atom concentrations given in Kelley *et al.*). These three specific ^{237}Np -affected locations are all downstream of PORTS. The DOE (2014) AESR report also reports ^{237}Np activities in sediments of Big Beaver and Big Run Creeks; these activities (in pCi/g) are similar to the atom concentrations (in pg/g) reported herein. ***It follows that the PORTS facility is the explanatory source of the elevated ^{237}Np concentrations in sediments downstream of the plant.***

Table 2 also reveals the existence of airborne pathways for release of non-fallout ^{237}Np , as elevated $^{237}\text{Np}/^{239}\text{Pu}$ ratios were also detected in attic dusts in at least one residence (Sample 40), and possibly, a second residence (Sample 34). The consistently low $^{239+240}\text{Pu}$ activities render it difficult, in some cases, to perform more precise $^{240}\text{Pu}/^{239}\text{Pu}$ measurements for further signature clarification.

It is also apparent that some of the soil samples (e.g., Sample 59) appear to resemble the $^{240}\text{Pu}/^{239}\text{Pu}$ expected fallout Np-Pu that is congruent with the Kelley *et al.* (1999) signatures; these soils lack any ^{237}Np elevation.

Table 2 also presents results for suspended sediments collected from an unnamed creek draining the “landfill construction area”. These samples exhibit very low $^{239+240}\text{Pu}$ activities, and also contain U that is indistinguishable from naturally occurring sources; nevertheless, it is evident (e.g., Samples 36, 38, 44, and 58) that these suspended samples consistently exhibit elevated $^{237}\text{Np}/^{239}\text{Pu}$ ratios that are not explainable via global (stratospheric) fallout. **The series of four sediment samples from the landfill drainage area were collected at different dates and under different flow/rain event conditions. These results point to a possible source of ^{237}Np in the landfill construction area.**

The above-mentioned ^{237}Np and $^{237}\text{Np}/^{239}\text{Pu}$ results can be viewed in the context of the Kelley *et al.* (1999) “null hypothesis” signature. It is evident that H_0 must be rejected for some of the samples presented in Table 2. Additional insight into the second source term is also obtained from Moody (1995). In Moody’s Table 5, absolute numbers of atoms per sample are reported for three samples from PORTS, and two samples from the Paducah Gaseous Diffusion Facility. The PORTS samples have only approximate ^{239}Pu and ^{240}Pu atom amounts reported; hence it is difficult to affix $^{237}\text{Np}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ signatures. Nevertheless, the three PORTS samples all point to a $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio of $\sim 300\text{--}400$, while the better-defined Paducah samples exhibit ratios of $\sim 900\text{--}1000$. It is also evident that the two Paducah samples, 94-7-38 and 94-7-45, both exhibit non-fallout $^{240}\text{Pu}/^{239}\text{Pu}$ of 0.065-0.070. These Paducah $^{240}\text{Pu}/^{239}\text{Pu}$ ratios are also very similar to the non-fallout $^{240}\text{Pu}/^{239}\text{Pu}$ we have measured in Little Beaver Creek sediments (Sample 46), along with a large elevation in $^{237}\text{Np}/^{239}\text{Pu}$.

The $^{237}\text{Np}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ results were used to construct a mixing diagram (Figure 6). Note that, because of the extreme variance in $^{237}\text{Np}/^{239}\text{Pu}$, the vertical axis has been plotted with a logarithmic scale; the Kelley NTS-stratospheric fallout mixing line therefore appears as a curved line at the bottom of the plot. Figure 6 illustrates that many of the samples shown in Table 2 are incongruent with the Kelley mixing line, even when precise $^{240}\text{Pu}/^{239}\text{Pu}$ ratios were not feasible (refer to the reported standard deviations in Table 2). It is obvious that a different component must be present. Given the Moody (1995) results, and the physical proximity of the samples to the PORTS facility, the results of Figure 6 indicate that the non-fallout ^{237}Np originates from PORTS. Our ^{237}Np results are consistent with statements made in DOE’s 2017 Monitoring Report (DOE, 2019).

Conclusions. To a reasonable degree of scientific certainty, the authors opine that **the PORTS facility is the source of the anthropogenic (enriched) uranium** found in the offsite environment. The PORTS facility, to a similar degree of reasonable scientific certainty, **is also the source of the non-fallout ^{237}Np and Pu, as well as the elevated Np atom concentrations encountered in the offsite environment.** These statements are based upon: i) the obvious deviations of the signatures from natural U and/or global fallout; ii) the explanation provided by the Moody signatures; iii) the presence of non-fallout ^{236}U as an indicator of “recycled U”, and iv) the absence of any other plausible local source that explains our observed results.

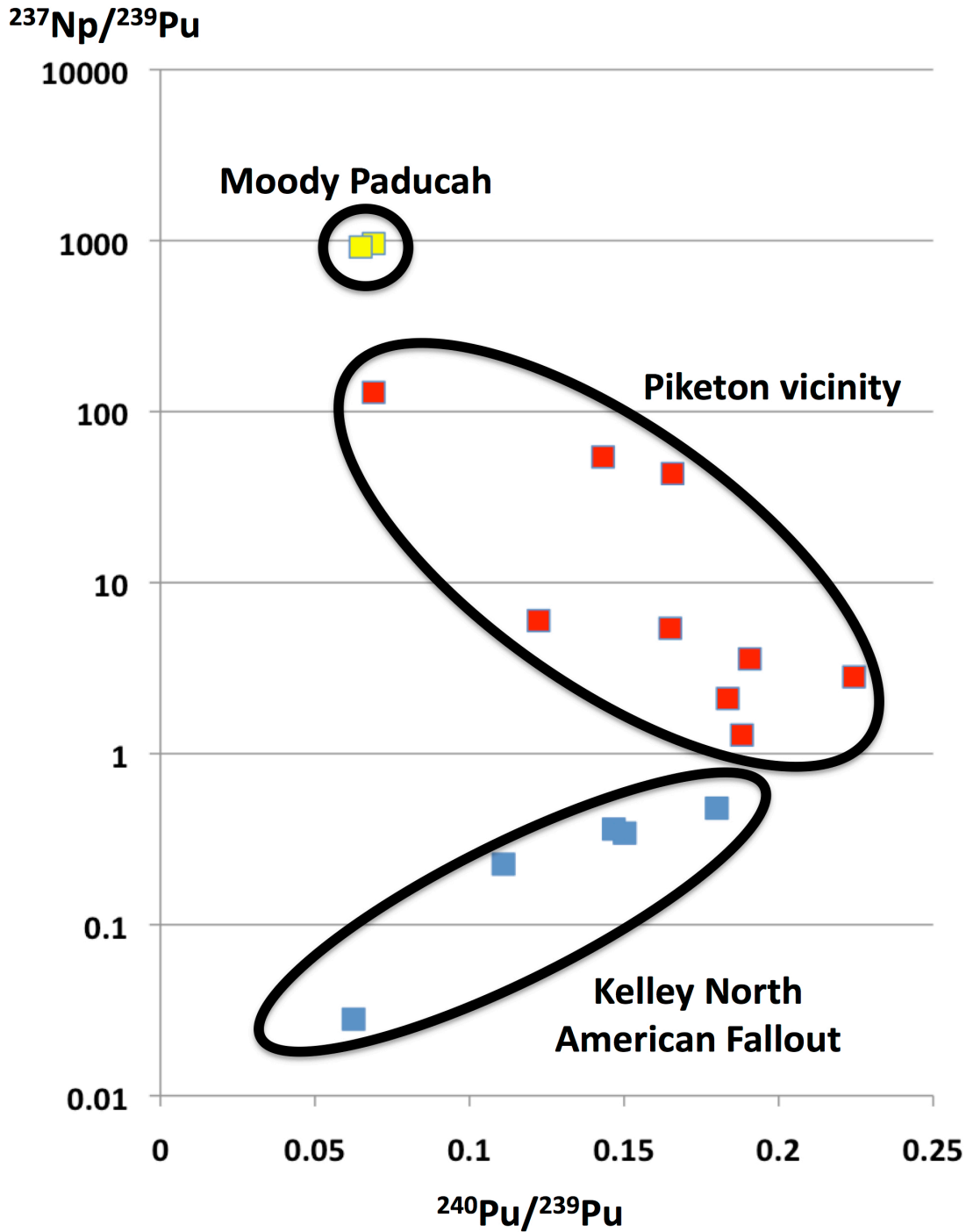


Figure 4. ^{237}Np - ^{239}Pu - ^{240}Pu mixing diagram, comparing the composition of North American nuclear weapons testing fallout (Kelley *et al.*, 1999; blue points), the samples Moody (1995; yellow points), and some of our Piketon-vicinity samples (red points). Note that the vertical scale is logarithmic; hence mixing lines appear as curved segments. On account of the low ^{240}Pu signals measured for many of our samples, the precision of many of the $^{240}\text{Pu}/^{239}\text{Pu}$ measurements is less than optimal (refer to Table 2); nevertheless, the Piketon-vicinity samples appear to plot along a hypothetical mixing curve with stratospheric fallout and Paducah end-members. Note that in the Kelley mixing curve, “stratospheric fallout” is at the upper right of the ellipse, and Nevada Test Site fallout appears at the lower left.

Table 1.

Sample	Description	234/238	234/238 sd	235/238	235/238 sd	236/238	236/238 sd
2	Little Beaver Creek (downstream) at Wakefield Mound Road	ND	ND	0.02597	3E-06	ND	ND
3	Big Beaver Creek (downstream) near Wakefield Mound Road	0.000220	2E-07	0.02520	3E-06	0.000094	2E-07
4	Big Beaver Creek (upstream) near Wakefield Mound Road	ND	ND	0.00719	4E-06	ND	ND
5	Unnamed Tributary to Scioto River	0.000149	1E-08	0.01846	8E-07	0.000055	4E-08
6	Big Run at Big Run Road and Tidd Hollow Road	ND	ND	0.01150	5E-06	ND	ND
7	Groundwater	ND	ND	0.00822	4E-06	ND	ND
8	Groundwater	ND	ND	0.00776	2E-06	ND	ND
9	Creek Sample from the landfill	0.000047	2E-08	0.00715	2E-07	0.000001	5E-09
11	Soil	0.000068	4E-08	0.00874	2E-07	0.000010	1E-08
12	Attic dust	0.000104	1E-07	0.01469	1E-06	0.000065	8E-08
13	Attic dust	ND	ND	0.00732	7E-07	ND	ND
14	Groundwater	ND	ND	0.00784	3E-06	ND	ND
15	Groundwater	ND	ND	0.00735	2E-06	ND	ND
16	Attic dust	0.000101	2E-07	0.01097	1E-06	0.000039	4E-08
17	Attic dust	ND	ND	0.01022	2E-06	ND	ND
18	Attic dust	0.000265	5E-07	0.02130	1E-06	0.000179	6E-08
18 rep	Attic dust	0.000278	7E-07	0.02024	6E-06	0.000186	1E-06
19	Attic dust	ND	ND	0.00719	4E-06	ND	ND
19 dup	Attic dust	0.000081	3E-06	0.01149	5E-05	0.000031	2E-06
20	Outbuilding	0.000112	3E-08	0.01185	7E-07	0.000047	7E-08
22	Soil	0.000056	1E-08	0.00747	5E-07	0.000003	2E-09
23	Groundwater	0.000077	6E-08	0.00742	1E-06	ND	ND
24	Schl sample 1	0.000062	5E-06	0.00767	2E-05	ND	ND
25	Schl sample 2	0.000060	5E-06	0.00723	8E-05	ND	ND
26	Schl sample 3	0.000064	2E-06	0.00789	2E-05	ND	ND
26 leach	Schl sample 3 leach	ND	ND	0.00881	5E-05	ND	ND
27	Schl sample 10	0.000057	2E-06	0.00715	9E-05	ND	ND
27 leach	Schl sample 10 leach	ND	ND	0.0075	1E-04	ND	ND
28	Schl sample 11	0.000056	4E-06	0.00739	2E-05	ND	ND
28 leach	Schl sample 11 leach	ND	ND	0.0075	1E-04	ND	ND
29	Schl sample 12	0.000057	2E-06	0.00719	2E-05	0.000005	2E-07
31	Attic dust 1	0.000076	1E-06	0.01026	6E-05	0.000025	3E-06
31 leach	Attic dust 1 leach	0.00010	1E-05	0.01333	4E-05	0.000044	6E-06

Table 1. (continued)

Sample	Description	234/238	234/238 sd	235/238	235/238 sd	236/238	236/238 sd
32	Outbuilding	ND	ND	0.00785	8E-05	ND	ND
33	Outbuilding	0.000102	6E-06	0.0119	1E-04	0.000033	3E-06
34	Outbuilding	0.000074	6E-06	0.00863	6E-05	0.000013	1E-06
37	Creek Sample from landfill	ND	ND	0.0074	1E-04	ND	ND
39	Attic dust	0.00014	2E-05	0.01797	4E-05	0.000062	3E-06
39 rep	Attic dust	0.000149	6E-06	0.01787	5E-05	0.000067	3E-06
40	Outbuilding	0.000095	4E-08	0.01055	1E-06	ND	ND
41	Little Beaver Cr (upstrm) at Bobo Rd	ND	ND	0.00785	6E-05	ND	ND
41 dup	Little Beaver Cr (upstrm) at Bobo Rd	0.000071	7E-06	0.0080	6E-04	ND	ND
42	Little Beaver Cr Sed (upstrm) at Bobo Rd	0.000065	2E-08	0.00717	7E-07	ND	ND
43	Creek Sample from landfill	ND	ND	0.0075	3E-04	ND	ND
44	Sed from Creek by landfill	0.000058	3E-09	0.00711	4E-07	ND	ND
45	Little Beaver Cr (dnstrm) at Wakefield Mound Rd	0.000198	1E-06	0.02236	9E-05	0.000075	1E-06
45 rep	Little Beaver Cr (dnstrm) at Wakefield Mound Rd	0.000207	6E-06	0.0233	1E-04	0.000070	1E-06
47	Big Beaver Cr (dnstrm) near Wakefield Mound Rd	0.000199	8E-07	0.0218	3E-04	0.000065	5E-06
47 dup	Big Beaver Cr (dnstrm) near Wakefield Mound Rd	0.000187	3E-06	0.0216	2E-04	0.00006	1E-05
48	Big Beaver Cr Sed (dnstrm) near Wakefield Mound Rd	0.000093	4E-08	0.01040	6E-07	0.000018	2E-08
49	Big Beaver Cr (upstrm) near Wakefield Mound Rd	ND	ND	0.0075	1E-04	ND	ND
50	Big Beaver Cr Sediment (upstream) near Wakefield Mound Rd	0.000055	3E-06	0.00714	5E-05	ND	ND
51	Unnamed Trib to Scioto River near Wakefield Mound Rd	0.00011	1E-05	0.0126	1E-04	0.000029	2E-06
52	Unnamed Trib to Scioto River Sed near Wakefield Mound Rd	0.000060	4E-06	0.00789	2E-05	ND	ND
53	Big Run at Big Run Rd and Tidd Hollow Rd	ND	ND	0.0134	1E-04	0.000029	2E-06
54	Big Run Sediment at Big Run Rd and Tidd Hollow Rd	0.000088	2E-06	0.01122	6E-05	0.000026	9E-07
55	2007 home attic dust	ND	ND	0.00798	9E-05	ND	ND
55 rep	2007 home attic dust	0.000061	4E-06	0.00799	2E-05	ND	ND
55 leach	2007 home attic dust	0.000062	2E-06	0.0084	2E-04	ND	ND
55 leach dup	2007 home attic dust	0.000070	4E-06	0.00841	4E-05	0.000016	9E-07
56	Attic dust	0.000079	3E-06	0.01060	2E-05	0.000029	5E-06
57	Creek Sample from landfill	ND	ND	0.0083	3E-04	0.00006	1E-05
58	Sed from Creek by landfill	0.000059	6E-06	0.00716	2E-05	0.000006	6E-07
59	Soil	0.000058	4E-08	0.00744	5E-07	0.000008	7E-09
60	Schl sample 13	0.000052	6E-08	0.00719	4E-07	0.000004	4E-09
65	Scioto River Dnstrm	0.00018	1E-05	0.01994	8E-05	0.000065	5E-06

Table 1. (continued)

Sample	Description	234/238	234/238 sd	235/238	235/238 sd	236/238	236/238 sd
65 dup	Scioto River Downstream	0.000202	5E-06	0.01973	5E-05	0.000059	3E-06
67	Scioto River Upstrm at Piketon boat ramp	0.000069	3E-06	0.00714	2E-05	ND	ND
69	Attic dust 2	0.000062	9E-06	0.0074	2E-04	ND	ND
69 leach	Attic dust 2 leach	0.000063	9E-06	0.00740	7E-05	ND	ND
72	Schl sample 5	0.000066	5E-06	0.0079	2E-04	ND	ND
73	Schl sample 6	0.000074	4E-06	0.00979	6E-05	ND	ND
73 dup	Schl sample 6 duplicate	0.000082	5E-06	0.0100	1E-04	ND	ND
74	Schl sample 7	0.000076	5E-06	0.0096	1E-04	ND	ND
75	Schl sample 8	0.000062	4E-06	0.00796	5E-05	ND	ND
76	Schl sample 9	0.000060	4E-06	0.0075	1E-04	ND	ND
76 dup	Schl sample 9 duplicate	0.000058	3E-06	0.00742	3E-05	ND	ND
77	2007 home attic dust	0.000071	5E-06	0.0090	2E-04	0.000012	2E-06
78	Little Beaver Cr (dnstrm) at Wakefield Mound Rd	0.00017	1E-05	0.0180	1E-04	0.000054	4E-06
79	Big Beaver Cr (dnstrm) near Wakefield Mound Rd	0.00014	2E-05	0.0170	2E-04	ND	ND
80	Unnamed Trib to Scioto River near Wakefield Mound Rd	0.00013	1E-05	0.0158	1E-04	0.000038	6E-06
81	Little Beaver Cr (upstrm) at Bobo Rd	ND	ND	0.0076	4E-04	ND	ND
82	Little Beaver Cr (dnstrm) at Wakefield Mound Rd	0.00020	1E-05	0.0227	1E-04	0.000065	5E-06
83	Big Beaver Cr (upstrm) near Wakefield Mound Rd	ND	ND	0.0077	3E-04	ND	ND
85	Unnamed Trib to Scioto River near Wakefield Mound Rd	0.000132	9E-06	0.0165	1E-04	0.000044	6E-06
94-7-14	Moody 1995 data, Portsmouth	0.000104	1E-08	0.01738	1E-06	0.000069	3E-09
94-7-17	Moody 1995 data, Portsmouth	0.000063	6E-09	0.01108	9E-07	0.000059	4E-08
94-7-19	Moody 1995 data, Portsmouth	0.000403	2E-08	0.03927	2E-06	0.000041	4E-09
94-7-38	Moody 1995 data, Paducah	0.000020	1E-09	0.00332	2E-07	0.000040	1E-08
94-7-45	Moody 1995 data, Paducah	0.000024	2E-09	0.00387	3E-07	0.000040	2E-08
Nat U	Moody 1995, natural U	0.000055		0.00725			

Table 2. Results for ^{237}Np atom concentrations (picograms per gram), $^{239+240}\text{Pu}$ activities (Bq/kg), and the atom ratios $^{237}\text{Np}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$; selected Piketon-vicinity samples were analyzed. The standard deviations (random error only) of each block of 3 to 5 sequential mass spectrometric measurements are shown. Note that large standard deviations are encountered for numerous $^{240}\text{Pu}/^{239}\text{Pu}$ results, on account of the relatively low activities and hence, low signal levels at ^{240}Pu . Further discussion of these results is beyond the scope/purpose of the present report.

Sample	Description	237/239	237/239 sd	240/239	240/239 sd	Bq/kg Pu	Bqkg sd	pg/g 237	pg/g sd
34	Barn dust sample	1.23	0.24	0.216	0.047	0.70	0.01	0.21	0.03
34 digest dup	Barn dust sample	1.18	0.21	0.202	0.085	0.85	0.14	0.25	0.03
36	Sediment, creek by landfill	1.29	0.29	0.188	0.062	0.05	0.01	0.02	0.00
38	Sediment, creek by landfill	2.10	0.15	0.184	0.051	0.14	0.01	0.07	0.01
40	Barn dust sample	2.81	0.33	0.224	0.055	0.27	0.02	0.18	0.01
42	Little Beaver Creek sediment, upstream	2.73	0.38	0.204	0.086	0.11	0.02	0.07	0.00
42 digest dup	Little Beaver Creek sediment, upstream	2.15	0.09	0.242	0.084	0.14	0.02	0.07	0.00
44	Sediment, creek by landfill	2.82	0.23	0.211	0.037	0.12	0.01	0.08	0.01
46	Little Beaver Creek sediment, downstream	129.53	1.40	0.069	0.002	1.27	0.03	56.55	0.88
48	Big Beaver Creek sediment, downstream	101.73	13.02	0.129	0.047	0.16	0.03	4.85	0.36
52	Scioto R Tributary near Wakefield Mound Rd.	6.00	2.00	0.122	0.042	0.04	0.02	0.07	0.00
54	Big Run sediment, Big Run/Tidd Hollow Rds.	5.41	0.36	0.165	0.029	0.10	0.01	0.15	0.01
58	Sediment, creek by landfill	3.58	1.92	0.191	0.127	0.05	0.02	0.04	0.01
59	Soil sample, residence	0.11	0.02	0.171	0.037	0.53	0.05	0.02	0.00
59 digest dup	Soil sample, residence	0.09	0.01	0.186	0.004	0.52	0.02	0.01	0.00
60	Soil sample, near local school	0.31	0.00	0.207	0.017	0.36	0.01	0.03	0.00
60 digest dup	Soil sample, near local school	0.33	0.01	0.189	0.037	0.36	0.03	0.03	0.00
61	Soil sample, near local school	0.37	0.08	0.200	0.083	0.25	0.02	0.02	0.00
62	Soil sample, residence	0.56	0.09	0.186	0.028	0.47	0.05	0.07	0.01
64	Soil sample, residence	0.49	0.11	0.217	0.068	0.05	0.00	0.01	0.00
66	Scioto River sediment, downstream	54.34	6.03	0.143	0.035	0.11	0.01	1.75	0.02
66 digest dup	Scioto River sediment, downstream	43.43	7.45	0.166	0.050	0.13	0.01	1.52	0.06
68	Scioto R sediment, upstream, boat ramp	0.58	0.06	0.267	0.039	0.06	0.00	0.01	0.00
70	Soil sample, residence	0.32	0.06	0.194	0.025	0.47	0.05	0.04	0.00

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Literature Cited

Bu, W.; Zheng, J.; Ketterer, M.E.; Hu, S.; Uchida, S.; Wang, X., Development and application of mass spectrometric techniques for ultra-trace determination of ²³⁶U in environmental samples-A review. *Analytica Chimica Acta* **2017**, 995, 1-20.

Kelley, J.M.; Bond L.A.; Beasley, T.M. "Global distribution of Pu isotopes and ²³⁷Np", *The Science of the Total Environment* **1999**, 237/238:483-500.

Ketterer, M.E.; Jordan, J.A.; Szechenyi, S.C.; Hudson, D.D., Layman, R.R., "Envirogeochemical Exploration for NORM Wastes: Quadrupole ICPMS Measurements of Thorium and Uranium Isotopes", *Journal of Analytical Atomic Spectrometry* **2000**, 15, 1569-1573.

Ketterer, M.E.; Wetzel, W.C.; Layman, R.R.; Matisoff, G.; Bonniwell, E.C., "Isotopic Studies of Sources of Uranium in Sediments of the Ashtabula River, Ohio, USA", *Environmental Science and Technology* **2000**, 34, 966-972.

Ketterer, M.E.; Hafer, K.M.; Link, C.L.; Royden, C.S.; Hartsock, W.J., "Anthropogenic ²³⁶U at Rocky Flats, Ashtabula River Harbor, and Mersey Estuary: Three Case Studies by Sector ICPMS", *Journal of Environmental Radioactivity* **2003**, 67, 191-206.

Ketterer, M.E., Hafer, K.M., Link, C.L., Kolwaite, D. Wilson, J., Mietelski, J.W., "Resolving global vs. local/regional Pu sources in the environment using sector ICPMS", *Journal of Analytical Atomic Spectrometry* **2004**, 19, 241-245.

Ketterer, M.E.; Szechenyi, S.C., "Review: Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences", *Spectrochimica Acta B* **2008**, 63, 719-737.

Ketterer, M.E.; Groves, A.D.; Strick, B.J.; Asplund, C.S.; Jones, V.J., "Deposition of ²³⁶U from atmospheric nuclear testing in Washington state (USA) and the Pechora region (Russian Arctic)", *Journal of Environmental Radioactivity* **2013**, 118, 143-149.

Lloyd, N.S.; Chenery, S.R.N.; Parrish, R.P., "The distribution of depleted uranium contamination in Colonie, NY, USA", Science of the Total Environment **2009**, 408, 397-407.

Moody, K.J., "Forensic Radiochemistry of PUBLIC Site Inspection Samples", Lawrence Livermore National Laboratory **1995**, UCRL-ID-119658.

US Department of Energy, "Student Summary of the US Department of Energy Portsmouth Annual Site Environmental Report (ASER) for 2014", **2014**, Office of Environmental Management Portsmouth/Paducah Project Office.

US Department of Energy, "Portsmouth Gaseous Diffusion Plant: Annual Site Environmental Report - 2017", **2019**, PPPO-03-5263593-19